Bond Strength of the Gold Alloy-Hydrothermal Ceramic Interface

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Summary

The aim of the study was to determine whether the rate of cooling induced structural changes in a high-gold alloy, and whether these changes modified the bond strength between the gold alloy and hydrothermal ceramic. Before ceramic firing, the casts were submitted to fast (water), normal (air) or slow (in the furnace) cooling. Three-point bending test was used in a total of 15 specimens of defined dimensions. The ultimate force at which ceramic detachment from the metal surface occurred and bending strength were determined. The values of coefficient (k) and surface (S) as factors in the assessment of bond quality were calculated. Photographs of the specimen microstructure were made and values of the microhardness of both materials determined. Analysis of variance (ANOVA) revealed no statistically significant difference in bond strength among the three types of specimens, suggesting that the mode of alloy cooling had no substantial effect either on the microstructure of the high-gold alloy or on the quality of bond between the gold alloy and hydrothermal ceramic.

Key words: *gold alloy, hydrothermal ceramic, bond strength.*

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Introduction

Fixed prosthodontics is a rehabilitation-restoration discipline of dental medicine dealing with the establishment of optimal occlusion, function, and esthetics. Unnatural metal color, inappropriate polymer properties, limited indications for initial ceramic, and high cost of gold alloys have imposed the need to search for new material combinations which would meet professional expectations concerning the strength, fit and esthetic effect, i.e. durability of the prosthetic appliance. The dental industry has responded in two ways, i.e. by a great variety of alloys, and by new ceramic materials (1-9). The choice of the metal-ceramic system depends primarily on knowledge of the alloy and ceramic composition, their compatibility according to the coefficient of thermal expansion, and optimal bond strength. Strength is the material property of resisting the interruption of its integrity. A number of tests are used to evaluate the bonding characteristics of a metal-ceramic system. Flexural tests allow for loading of the unilaterally or bilaterally fixed abutments. Three-point bending test according to Schwickerath, test according to Vos, and sliding test according to Schulmeyer and Schmitz are most widely used. Kelly and Rose advocate transverse bending, bending along the longitudinal axis of a flat metal bar with fired ceramic, and Shell-Nielsen traction test, whereas ADA recommends thermal expansion test, thermal shock, above mentioned three-point bending test, and multifold ceramic firing onto a wide-range construction for prognosis of the clinical success of the system (8). In the '90s, the Degunorm-Duceragold system appeared on the market (10,11). Degunorm is a precious, low--melting, yellow-colored gold alloy. It belongs to type IV hardness alloys and has a wide range of indications. Duceragold is a biphasic hydrothermal ceramic compatible with this alloy. Scholze et al. have found that hydroxyl groups can be incorporated into the glass matrix under certain conditions, thus improving the chemical properties of the glass, which becomes harder and its firing temperature is lower. As this incorporation is performed under heat and steam, the material thus obtained has been named hydrothermal glass. Leucyte crystals are considerably smaller and more evenly distributed than in feldspathic ceramic, therefore this type of ceramic material appears more homogeneous. The quality of a metal-ceramic system bonding strength depends on the microstructural properties of the interface between the two materials, and results from the metal surface preparation and the firing process of ceramic layers.

The purpose of the present study was to compare the quality of the bond between a high-gold alloy and hydrothermal ceramic in different conditions of metal cast cooling. Another aim was to assess changes in the structure, and thus in the microhardness of the metal upon ceramic firing.

Material and methods

A system consisting of Degunorm gold alloy (Degussa, Hanau, Germany) and Duceragold hydrothermal ceramic (Ducera Dental, Rosbach, Germany) was tested. Plates of 24x0.5x3 mm in size were formed in wax and invested in Neoduroterm investment (Bayern, Germany). The casts were made in a centrifugal casting machine (Krupp, Germany) at normal atmosphere. Different conditions, i.e. fast cooling by quenching the mold in water, slow cooling by leaving the mold in the furnace, and normal air cooling were used in five test pieces each. The cooled plates were sandblasted by 250-μm aluminum oxide abrasive to remove the investing material debris, then by fine sand of 110 μm. The above mentioned dimensions of the metal casts were obtained by additional treatment. The surface was steam cleaned at a pressure of 2 bars. The plates were oxidized for 5 min at 780°C in vacuum, followed by ceramic material firing to 1-mm thickness, and polishing. Thus prepared specimens were placed in a universal testing machine (VEB Thüringer Industriewerk, Germany). The specimens were centrally loaded by a conical pressure handpiece against the longitudinal axis of the specimen, at a loading speed of 7 mm/min and force of 3.7, 7.4, 11.1, and 14.8 to 59.2 N. Bending (s) and load (F) at which the ceramic broke away from the metal surface were measured. Five specimens were used for each parameter. The initial diagram slope relative to "p" axis, i.e. coefficient (k) of the line crossing the (0,0) and (F,p) points and calculated as $k = F/p$, was used as a criterion for evaluation of the ceramic-metal bond strength. The diagram presented in Fig. 1 allows for derivation of another characteristic used in the result analysis, i.e. the hatched area in the diagram, calculated as $S = F \times p/2$. Evaluation of strength was based on the fact that the metal-ceramic bond strength increases with the coefficient k decrease, i.e. the less slanted the initial segment of the diagram against "p" axis, the greater the S surface value. On statistical processing, the analysis of variance (ANOVA) at a 0.01 level of significance was used. Upon mechanical testing, the specimens were metallographically prepared according to recommendations for this type of material, including grinding, polishing, and etching in acid mixture. The specimen microstructure was photographed under a Leco 20001 light microscope, at 200x magnification. The values of micro-Vickershardness were determined at a 200-pound load, and statistically analyzed.

Results

Results are tabularly and graphically presented. Table 1 shows mean values (± standard deviation) of the specimen bending (p), applied force (F), calculated coefficient (k) and surface area (S) for all test pieces according to groups. The lowest bend before the ceramic layer detachment was measured in fast-cooled specimens (X = 0.12 ± 0.02), while the highest force before ceramic detachment was recorded in slow-cooled specimens (X = 13.46 ± ± 1.85), with a bending exceeding that measured in quenched specimens. The calculated values of k coefficient indicated the best and poorest bond to be achieved in the normally cooled (X = 72.54 ± ± 23.31) and quenched (X = 107.01 ± 25.45) test pieces, respectively. The highest value of S area was recorded for slow-cooled specimens, while air- and water-cooled specimens showed nearly identical S area values. The analysis of variance (ANOVA) yielded no statistically significant difference (p> >0.001) between the groups of specimens for any of the variables except for bending, which differed significantly between the water-cooled and all other specimens (Table 2). Graphic presentation of the results is shown in Figs. 2 and 3. Table 3, 4 and Figs 4 show calculated values of specimen microhardness according to groups, with a mean HV_{02} value of 195 for metal and 606 for ceramic. The specimen microstructure is presented in Figs. 5, 6 and 7. The fast-cooled specimens showed a high volume of porosity, as differentiated from low-volume and more evenly distributed porosity in the other two groups of slow-cooled specimens. Precipitated particles were visible along the grain margins in the fast-cooled ground specimen. These had visible precipitates along the border of the grains that were finer than in the other two sample groups. Analysis of the fracture character in all samples revealed detachment of the ceramic layer in all but one air-cooled specimen where a crack in the ceramic was observed.

Discussion

Bond strength between the metal surface and ceramic material is one of the crucial factors in technical, esthetic, and functional durability of a metal-ceramic appliance. Strength is expected to be exposed to bilateral effects. Gemalmaz et al. (12) observed metal construction distortion during the process of ceramic firing, whereas Fairhurst found microstructural changes modifying mechanical properties of the alloy to occur on ceramic firing, which could have affected the metal-ceramic bond (7). Živko et al. (13) conclude that the temperatures of ceramic firing are too low and the time too short for any substantial structural changes to occur, apart from negligible homogenization in the case of nonprecious alloys. Results of the present study revealed no significant differences in the high-gold alloy structure between the groups of test pieces. The slow-cooled cast with additional thermal treatment on ceramic firing is expected to have a more homogeneous structure with lower porosity. Higher porosity is expected in fast-cooled specimen, as confirmed in Fig. 7. Investigating the bond between metal and four ceramic materials from different manufacturers, Schäffer concludes that both interfaces, i.e. metal-ceramic and ceramic--ceramic, play a decisive role (14). Metal surface conditioning provides better bond strength results (15). Moorman et al. (16) recorded considerably higher values for the bond between high-gold alloy and feldspathic or low-fusing ceramic when the surface was conditioned with silicone ions. Rake et al. (17) report higher strength values when two layers of an opaque were applied onto nonoxidized Au-Pd alloy (without silver); with one-layer application, the alloy had to be oxidized. It has been demonstrated that the time and temperature of metal cast oxidation are equally important for optimal bond achievement. Insufficient oxide can be dissolved by ceramic, whereas oxide excess interferes with bonding chemistry. Therefore, removal of the oxide layer upon firing is recommended for Ni-Cr alloy (12, 18, 19). Schwickerath confirmed this by obtaining higher values of bond strength by sandblasting and ultrasonic cleaning of the metal cast, without oxidation (20). In contrast, Sauer believes that a thin layer of oxide does not compromise the bond, whereas sandblasting may contaminate the surface and interfere with bond strength (21). Baran demonstrated phasic alloy transformation near the ceramic interface, which implied alloy depletion of some elements. The third phase precipitation resulted from the matrix saturation with fusing elements that force the separation by creating the third phase. The matrix depletion is a consequence of metal surface heating and sandblasting (22). The samples that were not submitted to oxidation heating, did not show such a depletion even upon ceramic firing. Oxidation heating can also lead to changes in the values of the coefficient of thermal expansion, thus compromising the bond. Freesmeyer and Lindermann (23), McLean (24), and Okazaki et al. (25) advocate sandblasting of the metal surface, whereas others propose application of a gold layer for bond improvement. Nonprecious alloys as a rule must be cooled in the furnace to prevent ceramic contraction, which at the same time ensures higher bond strength. Jochen (cit. from ref. 8) measured higher bond strength in fast-cooled Pd--Ag alloy. All authors agree that polishing ensures higher stability of the metal-ceramic construction.

Three-point bending test was used by many authors for assessment of bond strength (8). Using this test, Pfeiffer et al. (26) demonstrated that the bend strength of particular ceramic layers declines from the opaque to the enamel layer. Küpper and Marx demonstrated a bend strength decline depending on the duration of the metal-ceramic titanium system stay in a corrosive bath and on the bath acidity (27). The unfavorable effect of thermocycling on the bond between silver-palladium alloy and hydrothermal ceramic has also been described (28, 29). Bengs and Keil believe that fast ceramic cooling leads to tension between the metal and ceramic, and propose slow ceramic cooling (cit. from ref. 8). Pang et al. (29) tested bond strength between Pd-Cu alloy and VMK-68 ceramic, cast titanium and Duceratin ceramic, and machine--milled titanium and Procera ceramic. Employing Schwickerath's test, they found a significantly higher bond strength between Pd-Cu alloy and VMK-68 ceramic (13.3 N), similar to our values, than in the other two systems (8.3 and 7.3 N). The same test was used by Yilmaz and Dincer, who calculated a fracture force of 25 N (30), whereas Papazoglou and Brantley observed no correlation between ceramic adhesion and load at fracture (31). Kappert et al. (32), and Küpper and Marx (27) report a force of 6.8 N and 18 N as the maximal load in the Ni-Cr alloy - ceramic system, respectively. Schwickerath describes slight differences in bond strength between precious and nonprecious alloys, whereas Voss and Meiers (33) and Eichner et al. (34) report a lower bond strength value for a combination of Ni-Cr alloys and ceramic as compared to precious alloy-ceramic systems. On comparison of six combinations of nonprecious alloys and ceramic, Lauš (8) recorded best S surface bonding for the Wiron 99-ceramic system (1.89 ± 0.12), while poorest bonding was observed for the Wiron 77-ceramic system (0.17 ± 0.02). Both these values are in high disagreement with those obtained for the same combination in the present study. In our study, higher values of force before low-fusing ceramic detachment from gold alloy were recorded, pointing to lower rigidity of this metal frame.

The use of different tests by various authors for the assessment of bond strength poses the problem of comparability of the results obtained. Schwickerath prefers flexural test for defined sample dimensions and test sequence, thus the results are comparable. The same author considers this test useful for determination of the force at which ceramic detachment from the metal surface occurs. Also, the test can answer the question of optimal metal surface treatment, bond quality, as well as the strength and elasticity of the alloy and ceramic.

Käppert et al. (35) propose that ultimate force for ceramic fracture depends on the metal plate flexibility or rigidity, i.e. on the product of multiplication of elasticity module and inertia momentum. This implies that the water-cooled specimens should be conditionally characterized by greatest rigidity. Persson and Bergman disagree with this statement, and consider that all tests only provide an insight into the bond strength, with no impact of the material rigidity (36). Finally, the question is whether the strength values obtained really express the quality of bond between the metal frame and ceramic or deviations in the specimen geometric dimensions, which should be discriminated in particular tests used.

Conclusions

1. The microstructure of high-gold alloy specimens submitted to different cooling procedures did not show any significant differences upon ceramic firing, apart from different volumes of porosity.
2. The values of microhardness were identical for the specimens subjected to different cooling procedures. There was a high difference in the value of microhardness between the alloy (HV_{02} = 195) and ceramic (HV_{02} = 606).

3. For the gold alloy-hydrothermal ceramic system, normal and slow cast cooling was found to be appropriate in terms of bond strength.
4. A statistically significant difference was recorded in the values of bending strength between quenched specimens and all other specimens.
5. The S value-based evaluation of the bond quality in the metal-ceramic system showed no statistically significant differences according to the metal frame cooling procedure. However, highest values were recorded for the slow-cooled specimens.
6. The choice and uniformity of specimen dimensions were definitely found to play a crucial role in the quality of bond strength, whereas the metal frame cooling procedure was of minor importance.
7. On the three-point bending test, fracture of the ceramic layer as a rule occurred at the moment of bond failure.

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